

FABRIC CLEANING SYSTEMField of the Invention

The present invention relates to a system for cleaning of
5 textile fabrics, namely to a method of such cleaning and also
compositions for carrying out that method. This system uses
densified carbon dioxide as the main component of the cleaning
liquor. As used herein, the term "densified carbon dioxide"
includes both liquid carbon dioxide and supercritical carbon
10 dioxide.

Background of the Invention

Conventionally, cleaning of textile fabrics such as clothes has
been effected either by an aqueous wash process or by dry
15 cleaning. The former method is performed either by hand or in
a machine. A detergent composition is dissolved in water to
create a wash liquor in which the fabrics are agitated. Then
the fabrics are rinsed in clean water and dried. In a
conventional dry cleaning process, the fabrics are first "pre-
20 spotted" using a soap or detergent bar and a small amount of
water to remove any visible stains. They are cleaned by
agitation in a body of an organic solvent, which is then
filtered and recycled for repeat use. The fabrics dry
relatively easily in view of the volatile nature of the
25 particular solvents which are normally used.

Conventional dry cleaning typically employs an organic solvent,
especially, perchlorethylene (PERC) is widely used to clean
fabrics. It is known to enhance PERC cleaning with surfactants
30 and other additives. One desirable class of additives comprises
fluorescers, sometimes also referred to as optical brighteners.

Fluorescers are used to give an enhanced appearance of
whiteness and/or cleanliness when the fabrics are viewed in

natural daylight. However, they have sometimes been used for their sunscreen properties to protect colours from fading and/or protect the skin of the wearer from sunburn. They are capable of this subsidiary use because their fluorescent
5 properties arise from the fact that they absorb ultra violet (UV) radiation and re-emit in the visible spectrum.

US-A-3 640 881 describes how a fluorescer pre-mixed with water can be incorporated in a PERC dry cleaning bath, the ratio of
10 PERC to the aqueous solution being high. A small amount of nonionic surfactant was also included. However, the amount of fluorescer delivered is relatively low. An object of the present invention was to provide a dry cleaning composition with a superior delivery of fluorescer to the fabric.

15 We have now found that by virtue of the present invention, a specific selection of fluorescers can be more efficiently delivered to fabrics in a dry cleaning process provided that the dry cleaning composition comprises carbon dioxide,
20 surfactant and small amounts of a polar solvent. Surprisingly, this has been found to be a more effective way of applying fluorescers during dry cleaning, then by the organic solvent route.

25 Some additives have been described for carbon dioxide dry cleaning. For example, it is known to enhance stain resistance to fabrics by using a fluoroacrylate polymer in the process, as described in WO-A-98/54397. Other optional additives are also mentioned. It has also been proposed to enhance cleaning
30 performance by including small amounts of water, particular surfactants and organic co-solvents, to form inverse micelles in the CO₂ medium. That is disclosed in WO-A-99/10585. For sizing or desizing yarns in the textile manufacturing industry,

it has been proposed to bring the textile into contact with adhesives, binders, waxes, lubricants, antioxidants, stickiness inhibitors and mixtures thereof whilst "wetting" the textile with liquid CO₂.

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Up to now, the carbon dioxide dry cleaning process has not proved to be capable of delivering fluorescers. The present invention solves this problem for the specific fluorescers described herein. Unexpectedly, this selection of fluorescers
10 as such is not compatible with carbon dioxide as it does not dissolve readily in the carbon dioxide. Accordingly, the present invention also encompasses a method of preparing a dry cleaning composition comprising said fluorescers.

15 Definition of the Invention

Thus, a first aspect of the present invention provides a dry cleaning composition comprising densified carbon dioxide and a polar solvent in a weight ratio of from 5:1 to 100,000:1, preferably from 10:1 to 10,000:1, and a hydrophilic fluorescer,
20 and a surfactant.

A second aspect of the present invention provides a method of dry cleaning a textile fabric by contacting a fabric with a composition according to the first aspect of the invention.

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A third aspect of the present invention provides a method of preparing a dry cleaning composition according to the first aspect of the invention, the method comprising preparing a premix of the fluorescer, surfactant and a polar solvent, and
30 optionally one or more of any other ingredients, admixing the premix with the densified carbon dioxide, and optionally any other remaining additional ingredients.

Detailed description of the invention

Recently, safety and environmental concerns have encouraged a search for an alternative dry cleaning method which does not
5 use organic solvents. This has led to a system which utilises densified, eg liquid, carbon dioxide as the dry cleaning medium. At normal atmospheric pressure, as it is cooled, carbon dioxide passes from the gaseous to the solid state without ever becoming a liquid. Therefore, it is necessary to
10 work in that part of the CO₂ phase diagram where it can exist in liquid or supercritical form. As a result, liquid CO₂ cleaning systems operate at an elevated pressure, typically about 50 times atmospheric pressure. The temperature is normally at or somewhat below ambient.

15 The method of fabric treatment with densified carbon dioxide comprises loading textile fabric, typically a variety of soiled articles, preferably clothing, into a vessel (preferably a pressurisable vessel) and contacting the articles with the
20 composition according the invention. The composition minus the densified carbon dioxide may be contacted with the soiled articles before or together with the carbon dioxide. The densified carbon dioxide may be introduced into the cleaning vessel as described in US-A-5,683,473. Preferably, the
25 densified carbon dioxide is introduced into the cleaning vessel which is then pressurised to a pressure in the range of about 0.1 to about 68.9 MPa and adjusted to a temperature range of from about -78.5°C up to about 30°C so that the carbon dioxide is in a liquid phase. Preferably the pressure range is from
30 0.5 to 48 MPa, more preferably from 2.1 to 41 MPa. Preferably, the temperature range is from -56.2 to 25°C, more preferably from -25°C to 20°C. After the cleaning step, the articles may be rinsed by introducing fresh carbon dioxide into the vessel

after removing the dry cleaning composition. In one preferred embodiment, the carbon dioxide in the inventive composition is in liquid form.

5 Surfactants

The composition according the invention comprises a surfactant. Any surfactant suitable for use in such a composition known to the person skilled in the art may be used. Suitable surfactants are, for example, described in US-A-5,789,505, US-A-5,683,977,
10 US-A-5,683,473, US-A-5,858,022 and WO 96/27704. Especially preferred are the surfactants described in WO 96/27704 (formulae I-IV) as discussed herein below.

The amount of surfactant is preferably sufficient to cause the
15 densified carbon dioxide, the polar solvent, with fluorescer and other optional components dissolved therein, to form a microemulsion. The amount of a given surfactant or surfactant blend to achieve this can readily be determined by persons skilled in the art, eg see Kaler, E.W. et al, *J. Phys. Chem.*,
20 1991, 95, 458-462; Fulton, J.L. et al, *J. Phys. Chem.*, 1989, 93, 4198-4204; Clarke M.J. et al, *J. Am. Chem Soc.*, 1997, 119, 6399-6406; and Eastoe J. et al, *Langmuir*, 1996, 12, 1423.

In a microemulsion, the droplets are too small to be observed by optical microscopy.

25

In general, a microemulsion of a polar solvent like water (with dissolved components) in densified carbon dioxide may be regarded as an emulsion in which the number average diameter of the water core (aqueous solution) droplets is from 2 nm to 10
30 nm.

Although an appropriate amount of surfactant is readily deducible for a given composition of the invention, using the techniques referred to above, typically the amount of total surfactant is from 0.001% to 20%, preferably from 0.01% to 10%,
5 more preferably from 0.03% to 5% by weight of the total composition, including the densified carbon dioxide.

The amount of polar solvent is typically also from 0.001% to 20%, preferably from, 0.01% to 10% especially from 0.03% to 5%
10 by weight of the total composition, including the densified carbon dioxide.

Further details of some preferred surfactants will now be given.

15 As used herein, the term "densified carbon dioxide-philic" in reference to surfactants R_nZ_m wherein n and m are each independently 1 to 50, means that the functional group, R_n- is soluble in carbon dioxide at pressures of from 101 kPa to 68.9
20 MPa and temperatures of from -78.5 to 100°C to greater than 10 weight percent. Preferably n and m are each independently 1-35. Such functional groups (R_n-) include halocarbons, polysiloxanes and branched polyalkylene oxides.

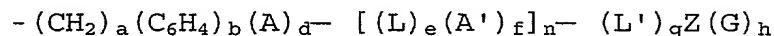
25 The term "densified carbon dioxide-phobic" in reference to surfactants, R_nZ_m , means that Z_m- will have a solubility in carbon dioxide of less than 10 weight percent at pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C. The functional groups in Z_m- include carboxylic acids,
30 phosphatyl esters, hydroxyls, C_{1-30} alkyls or alkenyls, polyalkylene oxides, branched polyalkylene oxides, carboxylates, C_{1-30} alkyl sulphonates, phosphates, glycerates,

carbohydrates, nitrates, substituted or unsubstituted aryls and sulphates.

The hydrocarbon and halocarbon containing surfactants (i.e.,
 5 R_nZ_m , containing the CO_2 -philic functional group, R_n- , and the CO_2 -phobic group, Z_m-) may have an HLB of less than 15, preferably less than 13 and most preferably less than 12.

The polymeric siloxane containing surfactants, R_nZ_m , also
 10 designated $MD_xD^*_yM$, with M representing trimethylsiloxyl end groups, D_x as a dimethylsiloxyl backbone (CO_2 -philic functional group) and D^*_y as one or more substituted methylsiloxyl groups substituted with CO_2 -phobic R or R' groups preferably have a $D_xD^*_y$ ratio of greater than 0.5:1, preferably greater than 0.7:1
 15 and most preferably greater than 1:1.

A "substituted methylsiloxyl group" is a methylsiloxyl group substituted with a CO_2 -phobic group R or R'. R or R' are each represented in the following formula:



wherein a is 1-30, b is 0-1, C_6H_4 is substituted or unsubstituted with a C_{1-10} alkyl or alkenyl and A, d, L, e, A',
 25 F, n L', g, Z, G and h are defined below, and mixtures of R and R'.

A "substituted aryl" is an aryl substituted with a C_{1-30} alkyl, alkenyl or hydroxyl, preferably a C_{1-20} alkyl or alkenyl.

30 A "substituted carbohydrate" is a carbohydrate substituted with a C_{1-10} alkyl or alkenyl, preferably a C_{1-5} alkyl.

The terms "polyalkylene oxide", "alkyl" and "alkenyl" each contain a carbon chain which may be either straight or branched unless otherwise stated.

5

A preferred surfactant which is effective for use in a composition according to the present invention requires the combination of densified carbon dioxide-philic functional groups with densified carbon dioxide-phobic functional groups (see definitions above). The resulting compound may form reversed micelles with the CO₂-philic functional groups extending into a continuous phase and the CO₂-phobic functional groups directed toward the centre of the micelle.

10 (see definitions above). The resulting compound may form reversed micelles with the CO₂-philic functional groups extending into a continuous phase and the CO₂-phobic functional groups directed toward the centre of the micelle.

15 The CO₂-philic moieties of the surfactants are groups exhibiting low Hildebrand solubility parameters, as described in Grant, D. J. W. et al. "Solubility Behavior of Organic Compounds", Techniques of Chemistry Series, J. Wiley & Sons, NY (1990) pp. 46-55 which describes the Hildebrand solubility equation,

20 herein incorporated by reference. These CO₂-philic moieties also exhibit low polarisability and some electron donating capability allowing them to be solubilised easily in densified fluid carbon dioxide.

25 As defined above the CO₂-philic functional groups are soluble in densified carbon dioxide to greater than 10 weight percent, preferably greater than 15 weight percent, at pressures of from 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C. Preferred densified CO₂-philic functional groups include

30 halocarbons (such as fluoro-, chloro- and fluoro-chlorocarbons), polysiloxanes and branched polyalkylene oxides.

The CO₂-phobic portion of the surfactant molecule is obtained either by a hydrophilic or a hydrophobic functional group which is less than 10 weight percent soluble in densified CO₂, preferably less than 5 wt. %, at a pressures of from 101 kPa to 5 68.9 MPa and temperatures of from -78.5 to 100°C. Examples of moieties contained in the CO₂-phobic groups include polyalkylene oxides, carboxylates, branched acrylate esters, C₁₋₃₀ hydrocarbons, aryls which are unsubstituted or substituted, sulphonates, glycerates, phosphates, sulphates and 10 carbohydrates. Especially preferred CO₂-phobic groups include C₂₋₂₀ straight chain or branched alkyls, polyalkylene oxides, glycerates, carboxylates, phosphates, sulphates and carbohydrates.

15 Preferred surfactants comprise CO₂-philic and CO₂-phobic groups. The CO₂-philic and CO₂-phobic groups are preferably directly connected or linked together via a linkage group. Such groups preferably include ester, keto, ether, amide, amine, thio, alkyl, alkenyl, fluoroalkyl, fluoroalkenyl and mixtures 20 thereof.

A generalised definition of preferred surfactants is represented in the general formula:

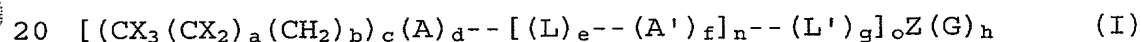
25 $R_n Z_m$

wherein R_n- is a densified CO₂-philic functional group, R is a halocarbon, a polysiloxane, or a branched polyalkylene oxide and n is 1-50, and Z_m- is a densified CO₂-phobic functional 30 group, and

m is 1-50 and at pressures of 101 kPa to 68.9 MPa and temperatures of from -78.5 to 100°C, the R_n- group is soluble in the densified carbon dioxide to greater than 10 wt. percent and the Z_m- group is soluble in the densified carbon dioxide to less than 10 wt. percent. It should be understood that R_n- and Z_m- may be present in any sequence, e.g. RZR, ZRZ, RRRZ, RRRZRZ etc. etc.

Preferably, when R of the surfactant is the halocarbon or the branched polyalkylene oxide, then the surfactant has an HLB value of less than 15. In other cases it may be preferred that when R is the polysiloxane, then the surfactant has a ratio of dimethyl siloxyl to substituted methyl siloxy groups of greater than 0.5:1.

Surfactants which are useful in the invention may be selected from four groups of compounds (general formulae I-IV). The first group of compounds has the formula (I):



wherein X is F, Cl, Br, I and mixtures thereof, preferably F and Cl;

a is 1 - 30, preferably 1-25, most preferably 5-20;

b is 0 - 5, preferably 0 - 3;

c is 1 - 5, preferably 1 - 3;

A and A' are each independently a linking moiety representing an ester, a keto, an ether, a thio, an amido, an amino, a C₁₋₄ fluoroalkyl, a C₁₋₄ fluoroalkenyl, a branched or straight chain polyalkylene oxide, a phosphato, a sulphonyl, a sulphate, an ammonium and mixtures thereof;

d is 0 or 1;

L and L' are each independently a C₁₋₃₀ straight chained or branched alkyl or alkenyl or an aryl which is unsubstituted or substituted and mixtures thereof;

e is 0-3;

5 f is 0 or 1;

n is 0-10, preferably 0-5, most preferably 0-3;

g is 0-3;

o is 0-5, preferably 0-3;

10 Z is a hydrogen, a carboxylic acid, a hydroxy, a phosphato, a phosphato ester, a sulphonyl, a sulphonate, a sulphate, a branched or straight-chained polyalkylene oxide, a nitryl, a glyceryl, an aryl unsubstituted or substituted with a C₁₋₃₀ alkyl or alkenyl, (preferably C₁₋₂₅ alkyl), a carbohydrate unsubstituted or substituted with a C₁₋₁₀ alkyl or alkenyl (preferably a C₁₋₅ alkyl) or an ammonium;

15 G is an anion or cation such as H⁺, Na⁺, Li⁺, K⁺, NH₄⁺, Ca⁺², Mg⁺²; Cl⁻, Br⁻, I⁻, mesylate, or tosylate; and h is 0-3, preferably 0-2.

20 Preferred compounds within the scope of the formula (I) include those having linking moieties A and A' which are each independently an ester, an ether, a thio, a polyalkylene oxide, an amido, an ammonium and mixtures thereof;

L and L' are each independently a C₁₋₂₅ straight chain or 25 branched alkyl or unsubstituted aryl; and Z is a hydrogen, carboxylic acid, hydroxyl, a phosphato, a sulphonyl, a sulphate, an ammonium, a polyalkylene oxide, or a carbohydrate, preferably unsubstituted. G groups which are preferred include H⁺, Li⁺, Na⁺, NH₄⁺, Cl⁻, Br⁻ and tosylate.

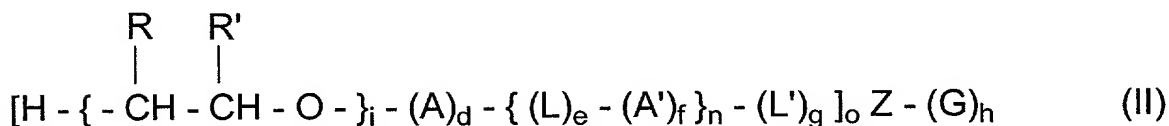
30 Most preferred compounds within the scope of formula (I) include those compounds wherein A and A' are each independently an ester, ether, an amido, a polyoxyalkylene oxide and mixtures

thereof; L and L' are each independently a C₁₋₂₀ straight chain or branched alkyl or an unsubstituted aryl; Z is a hydrogen, a phosphato, a sulphonyl, a carboxylic acid, a sulphate, a poly(alkylene oxide) and mixtures thereof; and G is H⁺, Na⁺ or
 5 NH₄⁺.

Compounds of formula (I) are prepared by any conventional preparation method known in the art such as the one described in March, J., "Advanced Organic Chemistry", J. Wiley & Sons, NY
 10 (1985).

Commercially available fluorinated compounds include compounds supplied as the ZonylTM series by Dupont.

15 The second group of surfactants useful in the inventive dry cleaning composition are those compounds having a polyalkylene moiety and having the general formula (II):



20

wherein R and R' each represent a hydrogen, a C₁₋₅ straight chained or branched alkyl or alkylene oxide and mixtures
 25 thereof;

i is 1 to 50, preferably 1 to 30, and

A, A', d, L, L', e f, n, g, o, Z, G and h are as defined above.

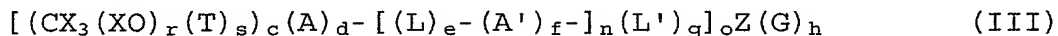
Preferably R and R' are each independently a hydrogen, a C₁₋₃ alkyl, or alkylene oxide and mixtures thereof.

Most preferably R and R' are each independently a hydrogen, C₁₋₃ alkyl and mixtures thereof. Non-limiting examples of compounds within the scope of formula (II) are described in WO 96/27704.

Compounds of formula (II) may be prepared as is known in the art and as described in March et al., *Supra*.

Examples of commercially available compounds of formula (II) may be obtained as the Pluronic series from BASF, Inc.

A third group of surfactants useful in the invention contain a fluorinated oxide moiety and the compounds have the general formula (III):



wherein XO is a halogenated alkylene oxide having C₁₋₆ straight or branched halocarbons, preferably C₁₋₃,

r is 1-50, preferably 1-25, most preferably 5-20,

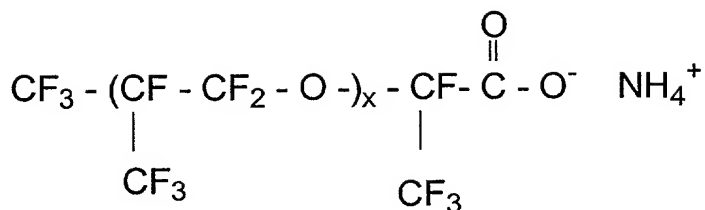
T is a straight chained or branched haloalkyl or

haloaryl,

s is 0 to 5, preferably 0-3, and

X, A, A', c, d, L, L', e, f, n, g, o, Z, G and h are as defined above.

Examples of commercially available compounds within the scope of formula (III) include those compounds supplied under the Krytox™ series by DuPont having a formula:



5 wherein x is 1-50.

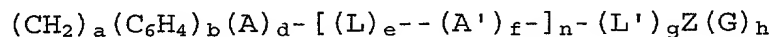
Other compounds within the scope of formula III are made as known in the art and described in March et al., Supra.

10 The fourth group of surfactants useful in the invention include siloxanes containing surfactants of general formula (IV):



15 wherein M is a trimethylsiloxyl end group, D_x is a dimethylsiloxyl backbone which is CO_2 -philic and D^*_y is one or more methylsiloxyl groups which are substituted with a CO_2 -phobic R or R' group,

 wherein R and R' each independently have the following
20 formula:



 wherein a is 1-30, preferably 1-25, most preferably 1-20,

25

b is 0 or 1,

C_6H_4 is unsubstituted or substituted with a C_{1-10} alkyl or alkenyl, and

A, A', d, L, e, f, n, L', g, Z, G and h are as defined above and mixtures of R and R' thereof.

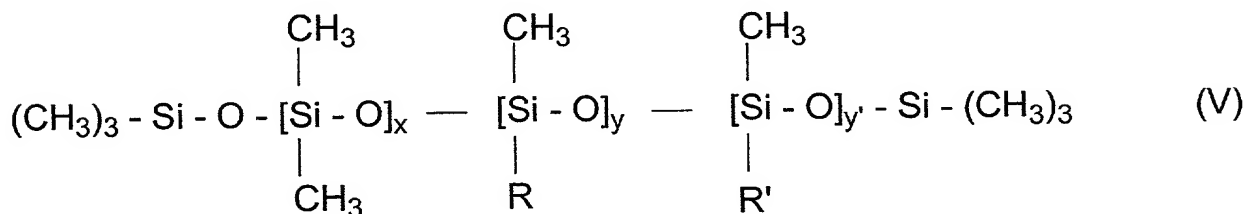
The $D_x:D_y$ ratio of the siloxane containing surfactants should be greater than 0.5:1, preferably greater than 0.7:1 and most preferably greater than 1:1.

The siloxane compounds should have a molecular weight ranging from 100 to 100,000, preferably 200 to 50,000, most preferably 500 to 35,000.

Silicones may be prepared by any conventional method such as the method described in Hardman, B. "Silicones" the *Encyclopedia of Polymer Science and Engineering*, v. 15, 2nd Ed., J. Wiley and Sons, NY, NY (1989).

Examples of commercially available siloxane containing compounds which may be used in the invention are those supplied under the ABIL series by Goldschmidt.

Suitable siloxane compounds within the scope of formula (IV) are compounds of formula (V):

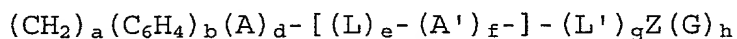


the ratio of $x:y$ and y' is greater than 0.5:1,

preferably greater than 0.7:1 and most preferably greater than 1:1, and

R and R' are as defined above.

- 5 Preferred CO₂-phobic groups represented by R and R' include those moieties of the following formula:



- 10 wherein a is 1-20,
b is 0,
C₆H₄ is unsubstituted,
A, A', d, L, e, f, n, g, Z, G and h are as defined
above, and mixtures of R and R'.

- 15 Particularly useful surfactants are selected from the group consisting of the classes of ethoxy modified polydimethylsiloxanes (e.g. Silwet™ surfactants from Witco), acetylenic glycol surfactants (from Air Products) and
20 ethoxy/propoxy block copolymers (e.g. Pluronic™ surfactants from BASF) and mixtures thereof.

Fluorescers

- The fluorescer component is selected from one or more
25 fluorescers, at least one of which is hydrophilic, i.e. water-soluble or water dispersible. A fluorescer is usually considered to be water-soluble or water dispersible when more than 0.1 g/L dissolves in demineralised water at 15°C. A more preferred selection of fluorescers can be described by their
30 log P value. Log P being the partitioning coefficient of the fluorescer between octanol and water at ambient temperature, whereby P is the concentration of the fluorescer in octanol divided by the concentration of fluorescer in water. (Leo et

al. Chem Rev 1971, 71, 525). If appropriate, the log P is determined in the presence of sodium and/or chloride as counterions. Accordingly, a preferred group of fluorescer is considered to be water soluble or water dispersible if it has a
5 log P of less than 2. It is noted that in many cases, the log P may also be estimated using specially designed programs, also described as clog P or calculated log P. However, if in certain cases these programs are inappropriate, the real log P should be measured.

10

In addition, a preferred group of surfactants can be described by the presence and pKa of certain functional groups in the fluorescer. Therefore, a preferred group of hydrophilic
fluorescers comprises fluorescers having at least one or more
15 Brönsted acidic, basic functional groups or mixtures thereof with a pKa of 7 or less. A Brönsted acidic functional group is generally defined as a -AH group having a pKa of 7 or less for the equilibrium dissociation constant $K_a = [-A^-][H^+]/[-AH]$. Likewise a Brönsted basic functional group is generally defined
20 as a -B group, the conjugate acid of it (i.e. BH^+) having a pKa of 7 or less for the equilibrium dissociation constant $K_a = [-B][H^+]/[-BH^+]$. Examples of acidic functional groups include sulphonate, carboxylate, sulphate, phosphate, phosphonate and phosphinate. Examples of basic functional groups include amino
25 groups, primary, secondary and tertiary amine groups.

Some preferred classes of hydrophilic fluorescers are those which are organic fluorescers having one or more hydrophilic groups independently selected from sulphonate, carboxylate,
30 sulphate, phosphate, phosphonate, phosphinate, hydroxyl, (primary, secondary and tertiary) amino and (poly)alkoxylated groups. Some preferred types include water-soluble and water-dispersible distyrylbiphenyl derivatives, distilbene

derivatives, coumarin derivatives, especially cyanuric chloride/diaminostilbene derivatives and dibenzofuranbiphenyl derivatives.

5 Optionally, one or more non-hydrophilic fluorescers may also be included, e.g. dissolved in the CO₂ continuous phase. However, this is less preferred. If present at all, the weight ratio of total hydrophilic fluorescer material to total non-hydrophilic fluorescer is from 100:1 to 1:100, preferably from 10:1 to 10 1:10, more preferably from 3:1 to 1:3. Usually, the hydrophilic component will exceed the non-hydrophilic.

Overall, the end concentration of fluorescer material in the dry cleaning composition is preferably from 0.1 to 1000ppm, 15 preferably from 0.5 to 500ppm, eg from 1 to 150ppm.

Hydrotrope

It is preferred to include a hydrotrope in the formulation. In the case of water-dispersible hydrophilic fluorescers, it is 20 helpful to incorporate the hydrotrope in the premix to ensure sufficiently fast dissolution of the premix in the carbon dioxide solvent. Preferably, the total hydrotrope content is from 0 to 90%, more preferably from 0.01 to 5%, more preferably, 0.05 to 2% by weight of the final composition.

25 Some preferred hydrotrope materials which may comprise all or part of the hydrotrope content are alkanols, especially C₁₋₄ alkanols such as ethanol, mono- di-, or triethanolamine and polyols such as glycols, e.g. mono- or diethylene glycol.

30 Modifiers

The dry cleaning composition may also be designed to include a modifier, such as water, or an organic solvent up to only about 10 wt%, and usual detergent additives to boost the cleaning

performance such as enzymes, surfactants, perfumes, whiteners and antistats, each up to about 10 wt%.

In a preferred embodiment, a modifier such as water, or a
5 useful organic solvent may be added with the stained cloth in the cleaning drum in a small volume. Preferred amounts of modifier should be from 0.0 to about 10 wt% (weight/weight of the densified CO₂), more preferably 0.001 to about 5 wt%, even more preferably 0.01 to about 3 wt%, most preferably from about
10 0.05 to about 0.2 wt%. Preferred solvents include water, ethanol, acetone, hexane, methanol, glycols, acetonitrile, C₁₋₁₀ alcohols and C₅₋₁₅ hydrocarbons and mixtures thereof. Especially preferred solvents include water, ethanol and methanol. If the modifier is water, optionally 0.1 to 50% of an additional
15 organic cosolvent may be present as described in US-A-5 858 022. In those circumstances it may be preferred to use surfactants as described in US-5 858 022 which do contain a CO₂ philic group.

20 Method of preparing a dry cleaning composition

The present invention also encompasses a method to prepare a dry cleaning composition, the method comprising preparing a premix of the fluorescer, surfactant and polar solvent, and optionally one or more of any other ingredients, admixing the
25 premix with the densified carbon dioxide, and optionally any other remaining additional ingredients. For some fluorescers it may be advantageous to adjust the pH of the premix to dissolve the fluorescers, e.g. some fluorescers dissolve at pH 4. Any polar solvent may be used that does not negatively affect the
30 dry cleaning process. In many cases it may be advantageous to use water, ethanol or mixtures thereof.

Other than in the examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about". Similarly, all percentages are weight/weight percentages of the carbon dioxide unless otherwise indicated. Molar ranges are weight per volume of carbon dioxide. Where the term comprising is used in the specification or claims, it is not intended to exclude any terms, steps or features not specifically recited.

10

Examples

The present invention will now be explained in more detail by way of the following non-limiting examples.

15 Example 1

A 1.00 g/l aqueous solution of Tinopal™ UNPA-GX (log P of less than 2) (Ex Ciba Geigy) was prepared. If the solution was turbid, it was titrated with triethanolamine (ca. 4.5g) until clear, to ensure the fluorescer was fully water-soluble.

20

This solutions were mixed in with equal parts by weight of Silwet™ L7620 surfactant (ex Witco™) (an ethyleneoxy modified polydimethylsiloxane and ethylene glycol. Ethylene glycol was added to reduce the viscosity of the mixtures.

25

End concentration in Premix

Fluorescer	0.333 g/kg
Surfactant	333 g/kg
Ethylene glycol	333 g/kg
Water	Balance

In each experiment, 3 g or 12 g of premix was put on the bottom of a stirred autoclave. Four white, fluorescer-free cotton swatches were put on the stirrer, the bottom of which acts as a plateau (the plateau prevents contact of the swatches with a premix). The 600 ml autoclave was filled with solvent: liquid CO₂ [at 5.52 Mpa]. The contents of the autoclave were stirred at 200 rpm for 15 mins.; T=12°C. Swatches were removed from the autoclave and allowed to dry.

- 10 Reflection spectra were recorded using an X-rite spectrophotometer model 968. (UV filter removed from spectrophotometer) The efficacy of fluorescer delivery was assessed by comparing the reflectivity at 440 nm, expressed as $DR(440) = R(440)_{\text{after treatment}} - R(440)_{\text{of untreated swatch}}$.
- 15 Averaged readings from 4 swatches were taken.

Concentrations of components in the dry cleaning composition:

Premix added	Fluorescer	Water g/l	Surfactant	EG
3 g	1.75 ppm	1.77 g/l	1.77 g/l	1.77 g/l
12 g	7.01 ppm	7.07 g/l	7.07 g/l	7.07 g/l

The results showed that an excellent improvement in reflectivity when the solvent was liquid CO₂.

Example C1.

The experiment as described in example 1 was repeated with perchlorethylene [at atmospheric pressure] instead of carbon dioxide as the solvent. The improvement in reflectivity of the carbon dioxide experiment was significantly better.

Example 2 and C2

Experiments as described under example 1 and C1 were repeated with TINOPAL™ CBS-X (comprising functional groups having a $pK_a < 7$) (Ex Ciba Geigy) as the fluorescer. The results again showed a better result using carbon dioxide as the solvent compared to 5 perchlorethylene.

Examples 3 and 4

The experiments described under example 1 and 2 respectively, were repeated whereby ethylene glycol was replaced by water.

10 Good results were obtained using either fluorescer.